Field assessment of the dynamics of particulate nitrate vaporization using differential TEOM® and automated nitrate monitors ☆

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Abstract

In this study, we report a comparison of the results from the differential tapered element oscillating microbalance (TEOM) and a semi-continuous nitrate monitor in an attempt to obtain insights into the dynamics of volatilization from the heated TEOM filter. Measurements were conducted in Claremont, California, a city downwind of Los Angeles and a region of high nitrate concentrations. Field results are compared with that obtained in the laboratory for sampling of pure ammonium nitrate aerosol, and with the vaporization losses predicted by theory. The primary hypothesis that we are testing is that the nitric acid and ammonia gas volatilization from particle-bound ammonium nitrate loaded on the TEOM's fiber filter occurs over time scales that are longer than the 5-min cycle time for the system. This is important to the use of the Differential TEOM, which utilizes the vaporization measured during alternate 5-min periods as a reference baseline value for its particle mass measurements.

Our experiments showed that under ambient conditions, the mass lost from the Differential TEOM tracks well the ambient particulate nitrate concentration. The saturation ratio for nitrate vapor immediately downstream of the filter, calculated at the filter temperature assuming all volatilized mass is ammonium nitrate, ranged from 0.05 to 0.2. By comparison, for laboratory collection of ammonium nitrate aerosol the vaporization reached a maximum value corresponding to a saturation of nitrate vapor downstream of the heated filter. This difference is due to the relatively higher particle concentrations used for the laboratory experiments. For the ambient measurements, the particulate nitrate concentrations were consistently lower than the equilibrium vapor concentration at the TEOM filter

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temperature. In both cases, the nitrate vaporization is driven by the temperature of the TEOM filter and independent of the pressure drop across the filter.

1. Introduction

Filtration is widely employed for the collection of ambient aerosols, including both integrated collectors and semi-continuous monitors. It has long been recognized that filter samples are subject to both negative and positive artifacts that arise from either the evaporative losses of volatile constituents or the adsorption of vapor constituents onto the filter media, or onto the particle deposit. For ammonium nitrate, evaporative losses of 50% or more are reported in both laboratory and field conditions (Appel et al., 1981; Wang and John, 1988; Zhang and McMurry, 1987, 1992; Cheng and Tsai, 1997; Hering and Cass, 1999). For organic constituents both positive and negative artifacts are reported. McDow and Huntzicker (1990), Turpin et al. (1994) and Kirchstetter et al. (2001) report excess organic carbon on quartz filters arising from the adsorption of vapor constituents. Eatough et al. (1996) report significant negative artifact from the evaporation of already deposited organic matter.

A number of methods are available to correct for these artifacts when collecting integrated filter samples for chemical analyses. Most commonly, a vapor denuder is used ahead of the particle collection filter to remove the positive artifact and an adsorbing filter behind the particle filter collects those aerosol constituents that volatilize during sampling.

Semi-continuous monitors for ambient particulate mass use filter collectors, with on-line determination of the deposited mass. For these instruments the correction for filter sampling artifacts is more complex than for filters that are assayed chemically. Federal standards specify that gravimetric mass is to be determined under standard environmental conditions. This is done to avoid the measurement of excess water that may be associated with the ambient aerosol. However, this requirement provides a complication for the semi-continuous instruments, which are not able to equilibrate samples at the prescribed humidity prior to determination of the deposited mass. To avoid the collection of water and to provide instrument stability, these instruments are generally heated to 30–50 °C. The heating can promote evaporative loss of volatile constituents such as nitrates and some organic matter that comprise the $PM_{2.5}$ mass.

The differential tapered element oscillating microbalance (Differential TEOM) has been developed to provide an artifact-corrected, real-time mass measurement (Patashnick et al., 2000; Jaques et al., 2003). This instrument is based on the more traditional TEOM monitor which collects particles on a small filter mounted at the top of an oscillating element, and determines the change in the filter mass through the change in resonant frequency of the oscillator. With the Differential TEOM, particles can be removed from the sample stream by means of an electrostatic precipitator. The precipitator is cycled on and off, providing alternate measurements of particle-laden ambient air and particle-free ambient air. The change in the collection filter mass obtained while collecting particle-free ambient air provides an internal reference, or baseline, for the mass change sensed while collecting ambient particulate. This approach is used to correct for both vaporization and adsorption artifacts associated with filter collection.

Reported here is a comparison of the results from the Differential TEOM monitor and a semi-continuous nitrate monitor. Measurements were conducted in Claremont, California, a city downwind of Los Angeles and a region of high nitrate concentrations. Field results are compared with those obtained in laboratory sampling of pure ammonium nitrate aerosol, and with the vaporization losses predicted by theory. The primary hypothesis that we are testing is that the nitric acid and ammonia gas volatilization from particle-bound ammonium nitrate collected on the TEOM monitor's fiber filter occurs over time scales that are longer than the 5-min cycle time for the system. This is important for the accuracy of the Differential TEOM, which utilizes the vaporization measured during alternate 5-minute periods as a reference baseline value for its particle mass measurements.

2. Experimental methods

A cascaded automated nitrate monitor and a Differential TEOM were collocated at Claremont, California from February 2002 to June 2002. Claremont is a receptor location, with relatively high concentrations of secondary air pollutant species, including ozone, nitric acid, sulfate, nitrate, and particulate organic carbon (Kim et al., 2000, 2002). These studies report a high fraction of $PM_{2.5}$ mass consists of labile species, such as ammonium nitrate and semiorganic compounds. Measurements were conducted as part of the Los Angeles

based US EPA sponsored Southern California Particle Center and Supersite (SCPCS).

The Differential TEOM® monitor (Patashnick et al., 2000; Jaques et al., 2002) employs an electrostatic precipitator to resolve artifactual changes in filter mass change related to semi-volatile PM. It is based on real-time, mass measurement capability of the TEOM mass monitor. Instead of sampling the ambient PM continuously, upstream of the TEOM mass sensor an electrostatic precipitator (ESP) was alternately switched on and off for 5 min periods. During the period when the ESP is switched off, the TEOM mass sensor samples the PM similar to a conventional TEOM monitor. During the periods when the ESP is switched on, the PM is removed from the sample stream and retrained by the ESP. During this ESP on period, any evaporation of collected PM or filter artifacts, such as gas adsorption or chemical reactions, are able to occur. The mass change of the filter with the ESP activated is subtracted from the mass change during the normal collection (with the ESP off) to provide an artifact-corrected net mass measurement.

The Differential TEOM monitor was configured to sample $PM_{2.5}$ aerosol, with a standard $16.67 \, L \, min^{-1}$ inlet followed by a sharp-cut cyclone. Of the inlet flow, $2 \, L \, min^{-1}$ is diverted into the heated, 13 mm-diameter filter for particle collection and mass measurement. The filter media was Pallflex TX40HI20-WW, a Teflon-coated glass fiber filter. Its temperature was held at $35 \, °C$ for the period from February (2002) to 3 June, 2002. Subsequent measurements were done with a filter temperature of $30 \, °C$. For the field campaign, the ESP was switched on and off every 5-min. During much of the study two-independent Differential TEOM systems were operated in parallel.

The cascaded Integrated Collection and Vaporization System (ICVS, Stolzenburg et al., 2003) measures nitrate with 10-min time resolution in three size fractions: 2.5–1.0, 1.0–0.5 and 0.5–0.08 μm. This system collects particles by impaction, using three impaction stages in series. Prior to collection particles are conditioned to $65 \pm 5\%$ RH to prevent particle bounce and to slow evaporative losses. Immediately after collection, the three sample deposits are analyzed immediately by flash-vaporization and subsequent catalytic reduction to NO, with detection by chemiluminescence. The collection time is 7.5 min, and the total cycle time, including analysis, is 10 min. Results from the Claremont site have compared well with filter data. The ADI monitor and the Harvard EPA Annular Denuder System (HEADS) $PM_{2.5}$ nitrate measurements, for which nitrate sampling artifacts are expected to be low, are well correlated ($r^2 = 0.79$) with a geometric mean ADI:HEADS ratio of 0.90 (Fine et al., 2003).

Laboratory studies with the Differential TEOM were conducted at SUNY Albany, as described by Schwab et al. (2003). The Differential TEOM was challenged with an ammonium nitrate aerosol, and its mass response was monitored during the period of the challenge, and for some hours subsequently. Ammonium nitrate test aerosol was generated using a spray atomizer (TSI 3076) followed by a neutralizer (TSI 3054) to remove excess electrical charge. The aerosol and particle-free dilution air is introduced into a horizontal 30 cm diameter × 6.4 m long glass slow-flow test chamber with a volume of approximately 450 L. For these experiments the relative humidity was held at approximately 5%, and the residence times in the chamber were 10–20 min. The Differential TEOM sampled at ports halfway down the flow tube chamber. Detailed description of the aerosol facility can be found in Schwab et al. (2003).

3. Results

Fig. 1 compares the hourly averaged signals from the Differential TEOM, both with and without the ESP activated, to the $PM_{2.5}$ nitrate concentration measured by the cascaded ICVC. During this period the TEOM filter lost mass whenever the precipitator was turned on, that is during periods of exposure to particle-free ambient air. To provide easy comparison with the nitrate concentration data, we have plotted the "vaporization reference", defined as the additive inverse of this value, namely the magnitude of the loss of mass from the Differential TEOM filter with the electrostatic precipitator activated. As is apparent, this vaporization reference signal tracks very well the $PM_{2.5}$ nitrate as measured by the cascaded ICVC system. For the data shown, the vaporization reference signal averaged $5.7 \, \mu g \, m^{-3}$ compared to mean value of $8.8 \, \mu g \, m^{-3}$ for the $PM_{2.5}$ nitrate, expressed as ammonium nitrate. Also shown is the TEOM mass, inferred as the difference between the signal with, and without particle collection. During this period the nitrate and its associated ammonium ion, comprised approximately 55% of the measured $PM_{2.5}$ mass.

Similar results are seen for the period of 23 May–3 June, as shown in Fig. 2. As before, we express the data in terms of the vaporization reference, equal to the negative of the Differential TEOM signal with the precipitator activated. Consistent with the data of Fig. 1, the vaporization reference signal tracks the ambient nitrate concentration. The mean mass lost with the electrostatic precipitator activated was 40% of the concentration of for $PM_{2.5}$ nitrate, expressed as ammonium nitrate. Throughout the study the data from the two collocated Differential TEOM monitors were well correlated, with regression coefficients of $R^2 = 0.89$ and 0.65 for $PM_{2.5}$ mass and vaporization reference signal, respectively.
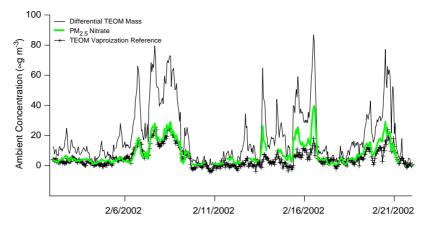
Fig. 1. Hourly $PM_{2.5}$ mass and vaporization reference signals from the mean of collocated Differential TEOM monitors, compared to hourly $PM_{2.5}$ nitrate measured with the cascaded ICVC system during a wintertime period of relatively high nitrate concentrations. The TEOM vaporization reference signal is the negative of the mass concentration measured during particle-free measurement cycle.
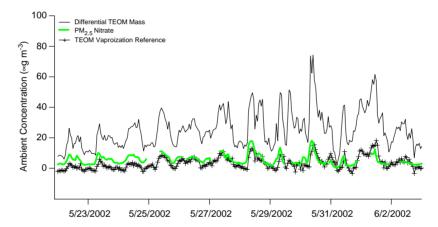

Fig. 2. Hourly $PM_{2.5}$ nitrate and Differential TEOM $PM_{2.5}$ mass and vaporization reference signals, as described for Fig. 1, for a period of relatively lower nitrate concentrations.

On some days, the Differential TEOM showed an increase in mass with the precipitator activated, i.e. while sampling particle-free ambient air. As shown in Fig. 3, the vaporization reference becomes negative, indicating a net adsorption of mass onto the TEOM filter during particle-free ambient air sampling. This signal is the same from both of the collocated Differential TEOMs, with the magnitude of the adsorption reaching $10\,\mu g\,m^{-3}$. These adsorption events were consistently observed at midday. We do not have an explanation on the timing of these events, but we chose to present the data to show that even during a period with nitrate PM present, the dominant artifact is not always the loss of nitrate through evaporation from the filter media.

For comparison, Fig. 4 shows results from the laboratory testing with a challenge of ammonium nitrate aerosol. Ammonium nitrate was introduced into the aerosol test chamber at a concentration of approximately $115\,\mu g\,m^{-3}$ over a period of several hours, at which time the aerosol generator was turned off. The Differential TEOM sampled the aerosol from the test chamber during the period of aerosol generation, and then continued to sample particle-free air for several hours after the aerosol generation was turned off. The Differential TEOM sample filter was clean at the outset, and held at a temperature of $30\,°C$ throughout. Traces are shown for the instrument response with and without the precipitator activated, and for the mass concentration calculated as the difference between these values. To provide easier comparison of the two traces, the particle-free air signal has not been multiplied by -1 and thus the vaporization loss from the filter shows here as a negative number. Within a few minutes the particle-free air signal reaches a relatively constant magnitude of $40\,\mu g\,m^{-3}$. After the aerosol generation was turned off
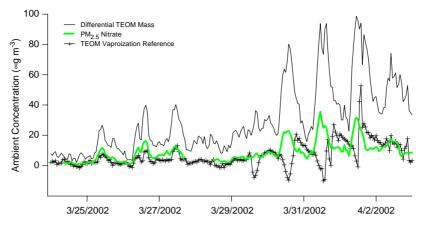
Fig. 3. Hourly $PM_{2.5}$ nitrate and Differential TEOM $PM_{2.5}$ mass and vaporization reference signals, as described for Fig. 1, for a period with vapor adsorption, shown as a negative vapor reference signal.
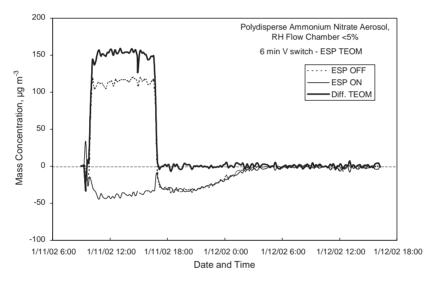

Fig. 4. Response of the Differential TEOM to laboratory-generated polydisperse ammonium nitrate aerosol. The TEOM was operated with a clean filter held at $30\,^{\circ}C$, and the precipitator was alternately switched on and off every 6 min. "ESP off" is the instrument response, (expressed as a mass concentration) while collecting aerosol, "ESP on" is the response for exposure to particle-free air, and "Diff. TEOM" is the measured mass concentration calculated as the difference of these two signals.

and the sampler was exposed to particle-free air, the signals with and without the precipitator activated are comparable, and the mass loss remains constant at nearly $30\,\mu g\,m^{-3}$ for several hours, eventually decreasing to zero once the nitrate was depleted from the collection filter.

4. Theoretical considerations

A critical aspect of the use of the particle-free ambient air measurement to correct for the inherent artifacts associated with the filter collection is the dynamics of the evaporative loss and vapor adsorption processes.

Evaporative loss from filters was first modeled by Zhang and McMurry (1987, 1991, 1992). They considered the case of the evaporative losses induced by the pressure drop through the filter with saturated vapor at the inlet, and showed that this loss increased from an initial value of zero to a maximum value equal to that required to produce saturated vapor downstream of the filter. Cheng and Tsai (1997) refined the theory of Zhang and McMurry, taking into account the increased pressure drop on a filter as it becomes loaded with particles. They showed that when challenged with an unsaturated air stream the initial loss from the filter is very rapid, similar to that for individual particles. As the filter loads, forming a bed of particles, the evaporation

from surrounding particles decreases the overall evaporation rate. Furuuchi et al. (2001) used the model of Zhang and McMurry, with refinements to account for noncontinuum particle evaporation and the changes over time in the particle distribution within the filter bed to describe their measurements of the evaporation of laboratory-generated ammonium nitrate PM from a TEOM a filter flushed with particle-free air.

In each of these models the rate of evaporation of mass from the filter is given by a simple mass balance

$$M_e = Q_2\rho_2 - Q_0\rho_0 \tag{1}$$

$$= Q_{of}\left[(\rho_2 - \rho_0) + \left(\frac{f-1}{f}\right)\rho_0\right], \tag{1b}$$

where

$$f = P_0 T_2 / P_2 T_0$$

and where ρ_0 and ρ_2 are the respective vapor concentrations upstream and downstream of the filter; Q_0 is the volumetric flow rate measured at the inlet temperature and pressures, T_0 and P_0, and $Q_2 = fQ_0$ is the volumetric flow rate at the downstream temperature and pressure, T_2 and P_2. Eq. (1b) has been explicitly formatted to show the two driving forces for the evaporative loss from the filters. These are: (1) the difference between saturation vapor pressure and the actual vapor pressure at the inlet of the filter, and (2) the decrease in the vapor pressure arising from the increase in the volumetric flow.

Zhang and McMurry modeled the evaporation for the isothermal case, with saturated vapor at the inlet of the filter, $\rho_0 = \rho_s$. Under these conditions the evaporative loss is given by the second term of Eq. (1b), wherein the pressure drop across the filter provides the driving force for evaporation of the deposited particles. The corresponding maximum evaporative loss is $M_e = Q_0\rho_s\Delta P/(P - \Delta P)$, which can be obtained by setting $\rho_2 = \rho_s, \rho_0 = \rho_s, P_2 = P_0 + \Delta P$ and $T_2 = T_0$ in Eq. (1b). For typical ambient conditions they found this equilibrium point is reached after about 1 hour of sampling.

The heating of the TEOM filter places this problem in a different regime than that modeled by Zhang and McMurry. The elevated temperature of the collection filter within the TEOM results in high values of the saturation vapor pressure ρ_s, and correspondingly low saturation conditions at the inlet of the filter. For dry ammonium nitrate aerosol the saturation vapor pressure, expressed in units of $\mu g\, m^{-3}$ is given by Mozurkewich (1993)

$$\Delta NO_3^- = \frac{745.7}{T}\exp\left(\frac{1}{2}\left(118.87 - \frac{24084}{T} - 6.025\ln T\right)\right), \tag{2}$$

where the temperature T is in Kelvin, and we have assumed equal molar ratio of ammonia and nitric acid.

At the $35\,°C$ operating temperatures of the TEOM filter, the equilibrium vapor pressure for nitric acid is $52\mu g\, m^{-3}$ (at equal molar ratios of nitric acid and ammonia). Ambient sampling temperatures ranged from 10 to $25\,°C$, which corresponds to equilibrium vapor pressures ranging from 2 to $16\mu g\, m^{-3}$. The net concentration difference is greater than $35\mu g\, m^{-3}$, which is large by comparison to 0.4–$3\mu g\, m^{-3}$ change resulting from the 0.2 atmosphere pressure drop across the TEOM filter. Unless the ambient temperature is within a few degrees of the TEOM temperature, the the evaporative losses are dominated by the change in the saturation vapor pressure due to the heating of the filter. For the heated TEOM filter the maximum rate of loss, achieved when the conditions downstream of the filter are saturated (i.e. when $\rho_2 = \rho_S$), is controlled by the first term of Eq. (1b), $Q_0 f(\rho_s - \rho_0)$.

Another significant point to note is that for the heated TEOM filter the equilibrium vapor pressure for volatilized nitrate generally exceeds ambient particulate levels. Thus for ambient sampling there is generally insufficient particle mass for the evaporative losses to be modeled by the equilibrium relation of Eq. (1). One must therefore consider the dynamics of the particle evaporative loss.

As described by Zhang and McMurry, the dynamics of particle evaporation from within the filter bed is governed by the mass conservation equation, where the gain in vapor mass per unit thickness of the filter is equated to the loss of particle mass within that incremental distance. In turn, the particle mass loss per unit length of filter is the product of rate of change in individual particle mass and the number concentration of deposited particles per unit depth within the filter. At the front of the filter the particle evaporation rate is controlled by the inlet saturation. As flow moves through the filter, the increase in vapor concentration from evaporation of the upstream particles tends to slow the particle evaporation rate, while any pressure drop within the filter bed tends to reduce the saturation and increase the evaporation. As argued above the pressure drop term is not significant for the heated TEOM filter.

Noting that the particle concentration declines exponentially with distance into the filter bed, the mass conservation equation that describes the vapor concentration within the heated TEOM filter can be written

$$\frac{dS}{dx'} = \tau e^{-\gamma x'}(1 - S) - \frac{dS}{dt'} \tag{3}$$

where influence of the pressure drop within the filter is ignored. Here $x' = x/L$ is the nondimensional distance through the filter, $S = \rho/\rho_s$ is the saturation ratio within the filter, $t' = tQ/AL$ is the nondimensional time and A and L are the filtration area and depth. Eq. (3) follows the formulation of Furuuchi et al., and uses the nondimensional time τ for filter loading, as defined by

Zhang and McMurry

$$\tau = 2\pi D_p g D C_N \gamma t, \tag{4}$$

where D_p is the particle diameter, D the diffusion coefficient, C_N the particle number concentration and t = sampling time. The factor γ describes the exponential decrease with distance in the distribution of collected particles within the filter, where the total filter penetration is given by $e^{-\gamma}$. The factor g is the ratio of the evaporation rate for an individual particle deposited on a filter to that of an isolated, airborne particle, and is included to account for the reduction in evaporation rate, and has a value somewhat less than 1 (Furuuchi et al., 2001).

It is important to note that for the case of insignificant pressure drop within the filter bed the driving force for particle evaporation is proportional to $(1 - S)$ and is largest at the front of the filter. In contrast, for the pressure-drop driven evaporation modeled by Zhang and McMurry, the driving force for evaporative losses depend on a term of the form $(x' - B')$, where B' is the ratio of the added vapor mass to that needed to provide saturation downstream of the filter. For their case the driving force for evaporation is zero at the front of the filter, and largest at the filter exit. This difference is significant when one considers that the concentration of particles deposited on the filter is largest at the front, decreasing exponentially through the filter bed. Thus one expects that the characteristic time for evaporation will be shorter for the heated filter than for the pressure-drop induced evaporative loss modeled by Zhang and McMurry.

Furuuchi et al. solved Eq. (3) for evaporative loss from the heated TEOM filter taking into account the variation of τ with time. They found that the time required to reach the maximum evaporative rate corresponds to a value of $\tau \cong 100$. In contrast, Zhang and McMurry found that the time to reach 90% of the maximum-vaporization rates at $\tau \cong 1000$. Thus the equilibration time for the heated filter, with negligible pressure drop, is approximately a factor of 10 times faster.

5. Comparisons with laboratory and field data

Comparison between the experimental data and these theoretical arguments is most easily addressed through the laboratory data of Fig. 4. During the period of particle exposure, the loss of mass from the TEOM filter when the electrostatic precipitator activated, normalized with respect to the flow rate through the filter, is $39 \,\mu g\, m^{-3}$. This is equivalent to a nitrate concentration of $30 \,\mu g\, m^{-3}$. For the $30\,°C$ operational temperature of the TEOM employed for these experiments the equilibrium vapor pressure of the dissociated ammonium

nitrate, expressed as nitrate, is $29.4 \,\mu g\, m^{-3}$. This shows that the volatilization rate reached a steady, maximum value equal to that required in order to attain vapor saturation downstream of the filter, in agreement with Zhang and McMurry, and with Eq. (1). Once the aerosol collection stopped, the evaporation rate was maintained at close to this value for several hours, until the accumulated mass dropped to near zero.

In the laboratory test the maximum loss rate was reached within two, 6-min cycles, or less than 12 min of total loading time on the filter. Assuming a filter efficiency of 99.3% $\gamma = 5$), an effective diffusion constant of $0.05\, cm^2\, s^{-1}$ (as given by Furuuchi et al.) and a particle nitrate size distribution having a volume geometric mean particle diameter of $0.4\,\mu m$ with geometric standard deviation of 1.8, then evaluation of Eq. (4) at the $114\,\mu g\, m^{-3}$ concentration for the laboratory aerosol yields $\tau/t \cong 0.4\, s^{-1}$. For the 12-min time period needed to reach the maximum, equilibrium vaporization loss rate the corresponding nondimensional time is $\tau \cong 200$. This is approximately a factor of 10 smaller than for the pressure-drop driven evaporation, and close to the value derived by Furuuchi et al.

For ambient measurements, data are summarized in Table 1 for five different measurement periods. These data include periods with valid data from all instruments, excluding three short periods that follow the pattern of Fig. 3, when vapor adsorption dominated. Shown are the ambient $PM_{2.5}$ nitrate concentration, the total $PM_{2.5}$ mass concentration, ambient and filter temperatures, and particulate nitrate mass median diameter taken from the cascaded ICVC system. The listed value for S is an upper limit for the saturation ratio of the flow exiting the TEOM filter calculated by attributing the vaporized mass entirely to ammonium nitrate, and adding to this the equilibrium nitric acid vapor concentration at ambient temperature (obtained with the assumption of equal molar ratios for ammonia and nitric acid).

As shown in Table 1, the downstream saturation ratio is between 0.1 and 0.6. Unlike the laboratory experiment described above, the vaporization reference signal from the Differential TEOM under ambient conditions does not reach saturation conditions. Instead, the vaporization tends to track the ambient nitrate concentration, as can be seen by inspection of the time series plots of Figs. 1 and 2. For the data presented in Table 1, the correlation between the hourly vaporization signal and the hourly ambient nitrate concentration gives $R^2 = 0.70$. Closer examination shows that the local maxima in the vaporization reference signal tends to lag behind the local maxima in the nitrate concentrations. Fig. 5 compares the vaporized mass concentration signals for the five data sets of Table 1 to the airborne nitrate concentration, offset by a 1-hour time lag. The

Table 1
Correlation between TEOM vaporization reference and ambient nitrate

Period	$PM_{2.5}$ mass ($\mu g\,m^{-3}$)	$PM_{2.5}$ Nitrate[a] ($\mu g\,m^{-3}$)	Vaporization[b] ($\mu g\,m^{-3}$)	Ambient Temperature (°C)	TEOM Filter Temperature (°C)	Saturation Ratio at exit of filter[c]	Nitrate MMD[d] (μm)	Offset[e] (min)	Correlation, R^2
3–13 February	18	6.9	5.4	14	35	0.16	0.54	40	0.94
19–29 March	14	5.0	3.6	15	35	0.14	0.63	40	0.75
23 May –3 June	26	5.7	3.6	19	35	0.20	0.86	70	0.67
6–9 June	33	7.8	6.8	22	30	0.56	0.75	100	0.69
27–31 August	28	4.5	1.6	23	30	0.48	0.83	80	0.67

[a]Measured by the ADI cascaded nitrate monitor.

[b]Estimated as the mass concentration lost during particle-free TEOM cycle.

[c]Estimated as mass concentration of nitric acid vapor at ambient temperature plus $0.8 \times$ vaporization mass divided by the nitrate saturation vapor pressure at the TEOM filter temperature, where the factor 0.8 is used to adjust the vaporized mass, assumed to be ammonium nitrate, to nitrate mass.

[d]Nitrate mass median diameter, estimated from the ADI cascaded nitrate monitor data.

[e]Defined as the difference in time between the local maxima of the vaporized mass and the continuous nitrate concentrations.
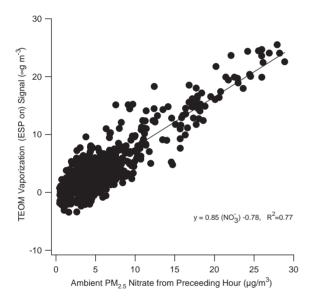

Fig. 5. Comparison of hourly averaged vaporization reference signal from the TEOM to the ambient particulate nitrate concentration from the preceding hour.

correlation is $R^2 = 0.77$ with a 1-hour delay applied to the ambient nitrate concentration.

To understand the time constant associated with this lag in more detail, regression analysis was performed for five separate periods during our study using the 10-min data. These results, summarized in Table 1, indicate that the time lag is shortest when the driving force, as indicated by the difference in equilibrium vapor pressures, is largest. For the wintertime data, with ambient temperatures of 14–15 °C, the highest correlation between the vaporization reference and the nitrate concentration corresponds to a lag in the vaporization

of 40 min. For the summer data, with ambient temperatures of 22–23 °C, and with the TEOM filter temperature reduced to 30 °C, this lag lengthens to 80–100 min.

Furuuchi et al. present calculations of the dependence of the nondimensional time, τ on the nondimensional evaporation rate, defined as the actual mass loss rate to that which gives saturation downstream of the filter. When the equilibrium vapor pressure at the filter temperature is significantly higher than the inlet vapor pressure, this nondimensional mass loss is given by the downstream saturation ratio S. For our data set, S was lower during first three periods, than in the final two periods, largely associated with the reduction in the temperature of the filter. Corresponding values of the nondimensional time for evaporation, taken from the results of Furuuchi et al. are $\tau \cong 7$ and $\tau \cong 30$ for these two regimes (i.e., for periods with filter at 35 and 30 °C, respectively). To obtain the corresponding characteristic time, the first moment of the size distribution, $D_p C_N$ is estimated from the measured mass median diameter of the nitrate aerosol obtained by the ICVC system of 0.7 μm aerodynamic diameter (0.6 μm Stokes diameter), and an assumed geometric standard deviation of 1.8 to give, from Eq. (4), a relationship for this data set of $t = 700\,\tau/NO_3^-$ s ($\mu g\,m^3$). Corresponding values for the characteristic time range from 10 to 20 min for the first three periods, and from 50 to 80 min for the final two periods. These values, estimated from the modeling results of Furuuchi et al. are close to the observed lag times of 40–100 min reported in Table 1. Both the modeling and experimental results are consistent in yielding longer times for higher downstream saturation ratio. In turn, the higher downstream saturation is found when the ambient temperatures are higher, and the TEOM filter is lower.

The above analyses indicate that the vaporization from the TEOM collection filter is not instantaneous,

$y = 0.85\,(NO_3^-) - 0.78,\quad R^2 = 0.77$

but has rather has a time constant between 10 and 100 min.Thus one would expect the loss measured in alternating 5-min time periods to be a good estimate of the vaporization losses during sampling under most circumstances. Ambient $PM_{2.5}$ mass concentrations reported by the Differential TEOM were found to agree within $\pm 10\%$ of the gravimetric mass measured by collocated filter and impactor samples, as reported by Jacques et al. (2004). This indicates that the vaporization reference signal measured in alternating 5-min intervals is indicative of the artifact during particle collection.

6. Conclusions

Under ambient conditions, the mass lost from the Differential TEOM when measuring particle-free air is observed to track the ambient particulate nitrate concentration. Mean saturation ratio immediately downstream of the collection filter ranged from 0.05 to 0.2. By comparison, for laboratory collection of ammonium nitrate aerosol, the vaporization reference signal reached a maximum value corresponding to a saturation of ammonium nitrate vapor downstream of the heated filter. In laboratory studies, the concentration of particulate nitrate was significantly higher than the vapor saturation concentration, while for the ambient measurements, the particulate nitrate concentration was consistently lower than the equilibrium vapor concentration at the TEOM temperature. Thus the ambient data correspond to much lower values of the dimensionless parameter τ defined by Zhang and McMurry that characterizes the vaporization as a function of the loading on the filter. In both cases, the nitrate vaporization is dominated by the temperature of the TEOM filter, and rather than the pressure drop across the filter.

Comparing the laboratory results with the field results shows that under controlled circumstances, the Differential TEOM monitor properly accounts for the levels of ammonium nitrate sampled. Under field conditions with varying concentrations of semi-volatile compounds, both evaporation and adsorption occurs simultaneously. The mass concentration reported by the Differential TEOM monitor self-corrects by determining the net effect of both of these physical phenomena. The results presented illustrate the ability of the Differential TEOM monitor to account for vaporization losses from the filter, and to correctly report the levels of PM mass present in the atmosphere.

Acknowledgements

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